

2000-182606

[Designation of Document] Specification

[Title of the Invention] Toner for the development of electrostatic image

[Claims]

1. A toner for the development of an electrostatic image wherein particulate resin is adhered or fixed over an agglomerate containing at least primary polymer particles, characterized in that said primary polymer particles have a structure substantially comprising a wax encapsulated therein.

2. The toner for the development of an electrostatic image according to claim 1, wherein said primary polymer particles are polymer particles obtained by seed polymerization with particulate wax as seed.

3. The toner for the development of an electrostatic image according to claim 2, wherein said particulate wax as the seed of the primary polymer particles has an average particle diameter of from 0.01 to 3 μm .

4. The toner for the development of an electrostatic image according to anyone of claims 1 to 3, wherein said particulate resin is resin particles obtained by seed polymerization with particulate wax as seed.

5. The toner for the development of an electrostatic image according to claim 4, wherein said particulate wax as the seed of the particulate resin has an average volume particle

diameter of from 0.01 to 1 μm .

6. The toner for the development of an electrostatic image according to anyone of claims 1 to 5, wherein said particulate resin has an average volume particle diameter of from 0.02 to 2 μm .

7. The toner for the development of an electrostatic image according to claim 4 or 5, characterized in that said particulate resin obtained by seed polymerization with particulate wax as seed is adhered or fixed to the agglomerate, and particulate resin containing no wax is further adhered or fixed thereon.

8. The toner for the development of an electrostatic image according to anyone of claims 1 to 7, wherein said primary polymer particles comprise a compound having a Brensted acidic group or a Brensted basic group as a polymerization unit.

9. The toner for the development of an electrostatic image according to anyone of claims 1 to 8, characterized in that said

primary polymer particles comprise said wax in an amount of from 1 to 40 parts by weight based on 100 parts by weight of a binder resin in the primary polymer particles.

10. The toner for the development of an electrostatic image according to anyone of claims 1 to 9, wherein said primary polymer particles have an average volume particle diameter of from 0.1 to 1 μm .

11. A method for producing a toner for the development of an electrostatic image, characterized in that a monomer mixture comprising a compound having a Brensted acidic group or a Brensted basic group is successively added in the presence of particulate wax to effect a seed emulsion polymerization, then, the resulting dispersion of the primary polymer particles is mixed with a dispersion comprising primary colorant particles and/or primary charge control agent particles to agglomerate the primary particles to form an agglomerate of the same, thereafter particulate resin having an average volume particle diameter of from 0.02 to 2 μm is adhered or fixed thereon.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention belongs]

The present invention relates to a toner for the development of an electrostatic image for use in electrophotographic process copying machines and printers. More particularly, the present invention relates to a toner for the development of an electrostatic image having excellent fixability, offset resistance, blocking resistance and charge ability.

[0002]

[Related Art]

A toner for the development of an electrostatic image

which has heretofore been widely used in electrophotography is prepared by a process which comprises melt-kneading a mixture of a styrene-acrylate copolymer, a binder resin such as polyester, a coloring agent such as carbon black and a pigment, a charge controller and/or a magnetic material through an extruder, grinding the material obtained, and then classifying the resulting powder. However, the conventional toner obtained by the foregoing melt-kneading/grinding process is disadvantageous in that the controllability of the particle diameter of the toner is limited, making it difficult to prepare a toner substantially having an average particle diameter of not more than 10 μm , particularly not more than 8 μm in a good yield. Thus, the conventional toner cannot be considered good enough to realize a high resolution which will be required in the future electrophotography.

[0003]

In order to achieve low temperature fixability, an approach involving the blend of a low softening wax in a toner during kneading has been proposed. In the kneading/crushing process, however, the amount of such a wax to be blended is limited to about 5%. Thus, toners having a sufficient low temperature fixability cannot be obtained.

In an attempt to overcome the difficulty in controlling the particle diameter and hence realize a high resolution,

JP-A-

63-186253 (The term "JP-A" as used herein means an "unexamined published Japanese patent application") proposes a process for the preparation of a toner involving emulsion polymerization/agglomeration process. However, this process too is limited in the amount of a wax to be introduced into the agglomeration step. Thus, this process leaves something to be desired in the improvement in low temperature fixability. Specifically, the present inventors have conducted investigations by increasing the addition amount of the wax on the basis of teach of the above-described patent. As the result, it could be found that with increasing the addition amount of the wax, such problems might occur that two peaks appeared in the particle size distribution of the resulting toner and finely divided powder having a particle diameter of 1 μm or less remained. Thus, after the agglomeration step, a classification step is indispensable.

[0004]

A process disclosed in JP-A-6-329947 involves the addition of an organic solvent infinitely soluble in water at the same time with the addition of a flocculating agent during the agglomeration step which allows the formation of agglomerated particles having a narrow particle diameter distribution. However, this process is disadvantageous in that it has many factors to be controlled and hence shows a poor reproducibility. This process is also disadvantageous

in that it gives a great burden of disposal of waste water.

Further, in JP-A-10-26842, is disclosed a so-called capsulated toner produced by agglomerating primary polymer particles obtained by emulsion polymerization, then fixing particulate resin on the surface of the resulting agglomerated particles. In this publication, a low temperature fixability and a high resolution are attempted to be achieved. However, sufficient performances are not necessarily obtained.

[0005]

[Problems that the Invention is to Solve]

It is therefore an object of the present invention to overcome the difficulties of the conventional toner for the development of an electrostatic image and hence provide a novel toner having a high resolution, and a sufficient low temperature fixability and offset resistance.

[0006]

[Means for Solving the Problems]

The present inventors have conducted extensive study and research efforts in order to solve the above-described problems. As the result, it could be found that the above-described problems could be solved by using primary polymer particles obtained by emulsion polymerization with wax emulsion as seed, and agglomerating a mixed dispersion including the primary polymer particles, thereafter encapsulating the resulting agglomerate with particulate resin. The present invention has

thus been worked out.

The essence of the present invention resides in a toner for the development of an electrostatic image wherein particulate resin is adhered or fixed on an agglomerate containing at least primary polymer particles, characterized in that the primary polymer particles have a structure substantially comprising a wax encapsulated therein.

[0007]

Another essence of the present invention resides in a method for producing a toner for the development of an electrostatic image, characterized in that a monomer mixture comprising a compound having an acidic polar group or a basic polar group is successively added in the presence of wax to effect a seed emulsion polymerization, then, the resulting dispersion of the primary polymer particles is mixed with a dispersion comprising primary colorant particles and/or primary charge control agent particles to agglomerate the primary particles to form an agglomerate of the same, thereafter particulate resin having an average volume particle diameter of from 0.02 to 2 μm is adhered or fixed thereon.

[0008]

[Mode for Carrying Out the Invention]

The present invention will be further described hereinafter.

As the wax to be used in the present invention, there

may be any known wax. Examples of such a wax include olefinic wax such as low molecular weight polyethylene, low molecular weight polypropylene and polyethylene copolymer; ester-based wax having long-chain aliphatic group such as paraffin wax, behenyl hehenate, montanic acid ester and stearyl stearate; vegetable wax such as hydrogenated castor oil and carbanaua wax; ketone having long-chain alkyl group such as distearyl ketone, higher aliphatic acid having alkyl group such as silicone and stearic acid; long-chain aliphatic acid alcohol; long-chain aliphatic acid-based polyvalent alcohol such as pentaerythritol, partial esterification product thereof; and higher aliphatic acid amide such as oleic acid amide and stearic acid amide.

[0009]

Among these waxes, those having a melting point of not higher than 100°C, preferably from 40°C to 90°C, particularly from 50°C to 80°C, are preferably used to improve the fixability of the toner. If the melting point of the wax exceeds 100°C, the resulting effect of lowering the fixing temperature of the toner is poor.

Further, ester-based waxes having long-chain aliphatic group are preferable and among these waxes, those having 20 to 60 carbon atoms are more preferable.

These waxes can be used alone or in any mixture thereof. Particularly, when ester-based waxes are used, plural kinds

of esters each having different number of carbon atoms are mixed and the mixture obtained is preferably used.

[0010]

One feature of the present invention resides in that primary polymer particles which will be explained below have a structure comprising wax encapsulated therein. The production method of primary polymer particles is not particularly limited as long as they have such a structure. However, a production method of primary polymer particles is preferably one wherein particulate wax is used for seed polymerization of resin.

The particulate wax employable herein can be obtained by the emulsification of the foregoing wax in the presence of at least an emulsifying agent selected from the group consisting of known cationic surface active agents, anionic surface active agents and nonionic surface active agents. Two or more of these surface active agents may be used in combination.

[0011]

Specific examples of the cationic surface active agent employable herein include dodecyl ammonium chloride, dodecyl ammonium bromide, dodecyl trimethyl ammonium bromide, dodecyl pyridinium chloride, dodecyl pyridinium bromide, and hexadecyl trimethyl ammonium bromide.

[0012]

Specific examples of the anionic surface active agent employable herein include aliphatic soap such as sodium stearate and sodium dodecanate, dodecyl sodium sulfate, sodium dodecylbenzenesulfonate, and sodium laurysulfate.

[0013]

Specific examples of the nonionic surface active agent employable herein include dodecyl polyoxyethylene ether, hexadecyl polyoxyethylene ether, nonylphenyl polyoxyethylene ether, lauryl polyoxyethylene ether, sorbitan monoleate polyoxyethylene ether, and monodecanoyl succrose.

[0014]

The average particle diameter of the particulate wax is preferably from 0.01 μm to 3 μm , more preferably from 0.03 μm to 1 μm , Particularly from 0.05 to 0.8 μm . For the measurement of average particle diameter, Microtrack UPA produced by NIKKISO Co., Ltd. may be used. If the average particle diameter of the particulate wax exceeds 3 μm , the polymer particles obtained by seed polymerization have too large an average particle diameter to provide a toner which can give a high resolution. On the contrary, if the average particle diameter of the particulate wax falls below 0.01 μm , the primary polymer particles obtained by seed polymerization have too low a wax content to sufficiently exert the effect of wax.

[0015]

In order to effect seed emulsion polymerization, a monomer having a Brensted acidic group (hereinafter, also referred to as simply acidic group) or a monomer having a Brensted basic group (hereinafter, also referred to as simply basic group) and a monomer having neither a Brensted acidic group nor a Brensted basic group (hereinafter, also referred to as other monomer) are successively added to cause polymerization in the emulsion containing particulate wax. During this procedure, these monomers may be separately added. Alternatively, a plurality of monomers may be previously mixed before added. Further, the composition of monomers to be added may be changed during addition. Moreover, these monomers may be added as they are or in the form of emulsion obtained by mixing with water or a surface active agent. As such a surface active agent there may be used one or more of the previously exemplified surface active agents.

During the progress of seed emulsion polymerization, a surface active agent may be added to the wax emulsion in a predetermined amount.

[0016]

The primary polymer particles obtained as described above substantially have a wax encapsulated therein. Referring to the morphology of the primary polymer particles, they may be of core-shell type, phase separation type,

occlusion type or the like. Alternatively, the primary polymer particles may be in the form of mixture of these morphologies. A particularly preferred morphology is core-shell type. The wax is normally used in an amount of from 1 to 40 parts by weight, preferably from 5 to 35 parts by weight, more preferably from 1 to 30 parts by weight based on 100 parts by weight of the binder resin used. Components other than wax such as a colorant and a charge control agent may be further used as seed so far as they don't depart from the scope of the present invention. Further, a colorant and a charge control agent dissolved or dispersed in wax can be used.

[0017]

Examples of the monomer having a Brensted acidic group employable in the present invention include monomers having carboxylic group such as acrylic acid, methacrylic acid, maleic acid, fumaric acid and cinnamic acid, monomers having sulfonic group such as styrene sulfonate, and monomers having sulfonic amide group such as benzene sulfon amide.

[0018]

Examples of the monomer having a Brensted basic group include aromatic vinyl compounds having amino group such as aminostyrene, monomers containing nitrogen-containing heterocycles such as vinylpyridine and vinylpyrrolidone; and (meth)acrylic acid esters having amino group such as dimethylaminoethyl acrylate and diethylaminoethyl

methacrylate.

Further, these monomer having acidic group and monomers having basic group can be present as salts with respective counter ions.

[0019]

Examples of the other monomers employable herein include styrenes such as styrene, methylstyrene, chlorostyrene, dichlorostyrene, p-tert-butylstyrene, p-n-butylstyrene and p-n-nonylstyrene, and (meth)acrylic acid esters such as methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, hydroxyethyl acrylate, ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, hydroxyethyl methacrylate and ethylhexyl methacrylate. Particularly preferred among these monomers are styrene, butyl acrylate, etc.

[0020]

These monomers may be used singly or in admixture. These monomers are preferably added such that the resulting polymer exhibits a glass transition temperature of from 40°C to 80°C. If the glass transition temperature of the polymer exceeds 80°C, the resulting toner exhibits too high a fixing temperature. Further, the resulting OHP transparency can be likely deteriorated. On the contrary, if the glass transition

temperature of the polymer falls below 40°C, the storage stability of the resulting toner is deteriorated to an extent such that problems can occur. As the monomer having an acidic polar group employable herein there is preferably used acrylic acid. As the other monomers employable herein there are preferably used styrene, acrylic acid ester and methacrylic acid ester.

[0021]

Examples of the polymerization initiator employable herein include persulfates such as potassium persulfate, sodium persulfate and ammonium persulfate, redox initiators obtained by combining these persulfates as one component with reducing agents such as acidic sodium sulfite, water-soluble polymerization initiators such as hydrogen peroxide. 4,4'-azobiscyanovaleric acid, t-butyl hydroperoxide and cumene hydroperoxide, redox initiators obtained by combining these water-soluble polymerization initiators as one component with reducing agents such as ferrous salt, benzoyl peroxide, and 2, 2'-azobis-isobutyronitrile. These polymerization initiators may be added before, at the same time with or after the addition of the monomers. These addition methods may be employed in combination.

[0022]

In the present invention, any known chain transfer agent

may be used as necessary. Specific examples of such a chain transfer agent include t-dodecyl mercaptan, 2-mercaptoethanol, diisopropyl xanthogen, carbon tetrachloride, and trichlorobromomethane. These chain transfer agents may be used singly or in combination. These chain transfer agents may be used in an amount of from 0 to 5% by weight based on the weight of the polymerizable monomers used.

[0023]

Further, the average particle diameter of the primary polymer particles is generally from 0.05 to 3 μm , preferably from 0.1 to 1 μm , more preferably from 0.1 to 0.5 μm . For the measurement of average particle diameter, for example, UPA may be used. If the particle diameter is less than 0.05 μm , the agglomeration rate is undesirably difficult to be controlled. While, If the particle diameter exceeds 3 μm , the toner obtained by agglomeration has too large a particle diameter to provide a toner which can give a high resolution.

[0024]

In accordance with the present invention, in preparing primary polymer particles, a colorant can be used with wax at the same time as seed. Alternatively, a colorant can be used by being dissolved or dispersed in wax. However, preferably primary polymer particles and primary colorant particles are simultaneously agglomerated to form an agglomerate, which is used as a core material of a toner. In such a case, primary

polymer particles comprising wax encapsulated therein are used. Depending upon the necessity, two or more kinds of primary polymer particles can be used. As the colorant employable herein there may be used any of inorganic or organic pigments and organic dyes, in combination as necessary.

[0025]

Specific examples of the colorant usable for primary colorant particles include known dyes and pigments such as carbon black, aniline blue, phthalocyanine blue, phthalocyanine green, hansa yellow, rhodamine dye or pigment, chrome yellow, quinacridone, benzidine yellow, rose bengal, triallylmethane dye, monoazo dye or pigment, disazo dye or pigment, and condensed azo dye or pigment. These dyes or pigments may be used singly or in admixture. If the toner of the present invention is a full-color toner, benzidine yellow, monoazo dye or pigment or condensed azo dye or pigment is preferably used as a yellow dye or pigment, quinacridone dye or pigment or monoazo dye or pigment is preferably used as a magenta dye or pigment, and phthalocyanine blue is preferably used as a cyan dye or pigment. The colorant is normally used in an amount of from 3 to 20 parts by weight based on 100 parts by weight of the binder resin used.

The colorant is used in the form of emulsion obtained by emulsifying in water in the presence of the emulsifying agent. The average particle diameter of the colorant employable herein

is preferably 0.01 to 3 μm .

[0026]

As the charge control agent, there may be used any known charge control agents, singly or in combination. Taking into account the adaptability to color toner (charge control agent itself is colorless or has a light color and hence doesn't impair the color tone of the toner), a quaternary ammonium salt compound is preferably used as a positively-charging charge control agent and a metal salt or metal complex of salicylic acid or alkylsalicylic acid with chromium, zinc or aluminum, a metal salt or metal complex of benzylic acid, amide compound, phenol compound, naphthol compound, phenolamide compound, and hydroxynaphthalene compound such as 4,4'-methylenebis[2-[N-(4-chlorophenyl)amide]-3-hydroxynaphthalene are preferably used as a negatively-charging charge control agent. The amount of the charge control agent to be used may be determined by a required electrified quantity of a toner. In practice, however, it is normally from 0.01 to 10 parts by weight, preferably from 0.1 to 10 parts by weight, based on 100 parts by weight of the binder resin used.

[0027]

In accordance with the present invention, as a method for including a charge control agent in a toner, mention may be made of a method wherein a charge control agent is used as seed together with wax in obtaining primary polymer particles,

a method wherein a charge control agent is used by being dissolved or dispersed in monomer or wax, and a method wherein primary polymer particles and a primary charge control agent particles are agglomerated at the same time to form an agglomerate, which is used as a toner. However, is preferably a method wherein before, during or after the process for adhering or fixing particulate resin, primary charge control agent particles are adhered or fixed. In this case, the charge control agent is also used as an emulsion in water having an average particle diameter of from 0.01 to 3 μm (primary charge control agent particles).

[0028]

In the production method of the toner of the present invention, one of preferable embodiments for obtaining an agglomerate (core material of toner) comprises mixing of respective emulsions of primary polymer particles comprising wax as seed, primary colorant particles, and primary charge control agent particles to agglomerate the same to form an agglomerate.

[0029]

Next, a feature of the present invention resides in that particulate resin is further coated (adhered or fixed) over the above-described agglomerate to form toner particles. As the particulate resin, those having a volume average particle diameter of preferably 0.02 to 2 μm , more preferably 0.05 to

1.5 μm , obtained by polymerizing the same monomer as the monomers used for the above-described primary polymer particles, can be used. The particulate resin is used as an emulsion obtained by dispersing the same with an emulsifier (the above-described surface active agent) in water or a liquid mainly comprising water. Particulate resin obtained by emulsion polymerization is preferably used.

Prior to coating the agglomerate with the particulate resin, the agglomerate can be fusion-bonded at a temperature of not less than the glass transition temperature of the primary polymer particles.

[0030]

The particulate resin can comprise wax or can be produced by emulsion polymerization using the above-described wax as seed. However, the outermost shell of a toner is preferably free from wax. Thus, in a case where an agglomerate is coated with particulate resin comprising wax, the coated surface is preferably further coated with particulate resin which does not comprise wax.

[0031]

The toner according to the present invention can be used with an additive such as fluidity improver as necessary. Specific examples of such a fluidity improver include hydrophobic silica powder, titanium oxide powder and aluminum oxide powder. Such a fluidity improver is normally used in

an amount of from 0.01 to 5 parts by weight, preferably from 0.1 to 3 parts by weight based on 100 parts by weight of the binder resin used.

[0032]

Further, the toner according to the present invention may have an inorganic particulate material such as magnetite, ferrite, cerium oxide, strontium titanate and electrically conductive titania or a resistivity adjustor or lubricant such as styrene resin and acrylic resin incorporated therein as an internal or external additive. The amount of such an additive to be added may be properly predetermined depending on the desired properties. In practice, however, it is preferably from 0.05 to 10 parts by weight based on 100 parts by weight of the binder resin used.

[0033]

The toner for the development of an electrostatic image of the present invention may be in the form of either two-component developer or non-magnetic one-component developer. The toner of the present invention, if used as a two-component developer, may have any known carrier such as magnetic material such as iron powder, magnetite powder, ferrite powder, material obtained by coating the surface of such a magnetic material with a resin and magnetic carrier. As the coating resin to

be used in the resin-coated carrier there may be used generally known resins such as styrene resin, acrylic resin, styrene-acryl copolymer resin, silicone resin, modified silicone resin, fluororesin or mixture thereof.

[0034]

[Examples]

The present invention will be further described in the following examples.

The term "parts" as used hereinafter is meant to indicate "parts by weight". For the measurement of the average particle diameter, molecular weight, glass transition point (Tg), fixing temperature width and electrified quantity of the polymer particles, the following methods were used.

[0035]

Average particle diameter: UPA produced by Microtrack K.K. or Coal Tar Counter Multisizer II model (abbreviated as Coal Tar Counter) produced by Coal Tar Inc. was used.

Weight-average molecular weight: Gel permeation chromatography (GPC) was employed. (Solvent: THF; calibration curve: standard polystyrene)

Glass transition point (Tg): DSC 7 produced by Perkin Elmer Inc. was used.

[0036]

Fixing temperature width: A recording paper having an unfixed toner image supported thereon was prepared. The

recording paper was carried into the fixing nip during which the surface temperature of heated rolls was varied from 100°C to 220°C. The recording paper discharged from the fixing nip was then observed for fixing conditions. The temperature range within which the heated rolls undergo no toner offset during fixing and the toner which has been fixed to the recording paper was sufficiently bonded to the recording paper was defined as fixing temperature range. The heated rolls in the fixing machine has a releasing layer made of PFA (tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer). Evaluation was effected under such a condition that the nip width was predetermined to 4 mm without coating silicone oil, and a fixing rates were 120 mm/s and 30 mm/s.

[0037]

Electrified quantity: A toner was charged into a non-magnetic one-component developer tank (Color Page Presto N4 developer tank, manufactured by Kasio K.K. or Phaser 550 developer tank, produced by Kyushu Matsushita K.K.), then rollers were revolved for a predetermined period, thereafter, the toner on the roller was sucked. An electrified quantity per unit weight was determined from the electrified quantity and the weight of the sucked toner.

[0038]

<Preparation of wax dispersion>

As 100 parts amount of a wax dispersion, 30 parts of

behenyl behenate was emulsified in the presence of 1.67 parts of sodium N-dodecylbenzene sulfonate by applying high pressure shearing to obtain the dispersion of ester wax. The solid concentration of the resulting dispersion was 30% and the dispersion had an average particle diameter determined by UPA of 220 nm (wax dispersion A).

[0039]

As 100 parts amount of a wax dispersion, 30 parts of behenyl behenate was emulsified in the presence of 0.23 part of sodium N-dodecylbenzene sulfonate by applying high pressure shearing to obtain the dispersion of ester wax. The solid concentration of the resulting dispersion was 30% and the dispersion had an average particle diameter determined by UPA of 400 nm (wax dispersion B).

[0040]

<Preparation of primary polymer particle dispersion>

Into a glass reaction vessel equipped with an agitator, a heating condenser, a concentrating apparatus and an apparatus for charging starting materials and auxiliaries were charged wax dispersion A 35 parts and desalted water 400 parts, which were then heated to a temperature of 90°C in a flow of nitrogen.

Thereafter, to the mixture obtained were added the following monomers, an aqueous solution of an emulsifier and polymerization initiators. The reaction mixture was then allowed to undergo emulsion polymerization for 6.5 hours.

[0041]

[Table 1]

(Monomers)

Styrene	79 parts
Butyl acrylate	21 parts
Acrylic acid	3 parts
Octane thiol	0.38 part
Hexanediol diacrylate (HDDA)	0.7 part
(Aqueous solution of emulsifier)	
Aqueous 10% sodium N-dodecylbenzene sulfonate (S-DBS)	1 part
Desalted water	25 parts
(Polymerization Initiator)	
8% aqueous hydrogen peroxide	10.6 parts
8% aqueous ascorbic acid	10.6 parts

[0042]

After the completion of the polymerization reaction, the resulting product was cooled to obtain an opaque white polymer dispersion. The polymer dispersion thus obtained had a weight-average molecular weight of 98,000, an average particle diameter determined by UPA of 190 nm and Tg of 57°C. The section of the resulting emulsion was observed by TEM. It was observed that the wax was encapsulated with the resin (primary polymer particle dispersion A).

[0043]

An opaque white polymer dispersion was obtained as in the primary polymer particle dispersion A except that the wax dispersion B was used instead of the wax dispersion A and monomers were changed as described below. The resulting polymer dispersion had the weight average molecular weight of 71,000, the average particle diameter determined by UPA of 179 nm, and Tg of 48°C (primary polymer particle dispersion B).
[0044]

[Table 2]

(Monomers)

Styrene	64 parts
Butyl acrylate	36 parts
Acrylic acid	3 parts
Divinyl benzene (DVA)	1 part
Trichlorobromomethane	0.5 part

[0045]

An opaque white polymer dispersion was obtained as in the primary polymer particle dispersion B except that the amount of styrene was changed to 67 parts and the amount of butyl acrylate was changed to 33 parts. The resulting polymer dispersion had the weight average molecular weight of 52,000, the average particle diameter determined by UPA of 205 nm, and Tg of 51°C (primary polymer particle dispersion C).

[0046]

An opaque white polymer dispersion was obtained as in

the primary polymer particle dispersion B except that the amount of styrene was changed to 72 parts and the amount of butyl acrylate was changed to 28 parts. The resulting polymer dispersion had the weight average molecular weight of 44,000, the average particle diameter determined by UPA of 158 nm, and Tg of 55°C (primary polymer particle dispersion D).

[0047]

<Preparation of particulate resin dispersion>

Into a glass reaction vessel equipped with an agitator, a heating condenser, a concentrating apparatus and an apparatus for charging starting materials and auxiliaries were charged 10% aqueous solution of S-DBS 4.3 parts and desalted water 400 parts, which were then heated to a temperature of 90°C in a flow of nitrogen.

Thereafter, to the mixture obtained were added the following monomers, an aqueous solution of an emulsifier and polymerization initiators. The resulting reaction mixture was then allowed to undergo emulsion polymerization for 6.5 hours.

[0048]

[Table 3]

(Monomers)

Styrene	79 parts
Butyl acrylate	21 parts
Acrylic acid	3 parts

Trichlorobromomethane	0.5 part
DVB	0.4 part
(Aqueous solution of emulsifier)	
Aqueous 10% S-DBS solution	2.2 parts
Desalted water	25 parts
(Polymerization Initiator)	
8% aqueous hydrogen peroxide	10.6 parts
8% aqueous ascorbic acid	10.6 parts

[0049]

After the completion of the polymerization reaction, the resulting product was cooled to obtain an opaque white polymer dispersion. The polymer dispersion thus obtained had a weight-average molecular weight of 110,000, an average particle diameter determined by UPA of 120 nm and Tg of 86°C (particulate resin dispersion A).

[0050]

An opaque white polymer dispersion was obtained as in the particulate resin dispersion A except that DVB was not used. The resulting polymer dispersion had the average particle diameter determined by UPA of 154 nm, and Tg of 65°C (particulate resin dispersion B).

[0051]

<Preparation of particulate colorant dispersion>

As 100 parts amount of a particulate colorant dispersion, 30 parts of pigment blue 15:3 was dispersed in the presence

of 5 parts of polyoxyethylene alkylphenyl ether by means of a sand grinder mill to obtain the particulate colorant dispersion. The resulting dispersion had a solid concentration of 35%, and an average particle diameter determined by UPA of 150 nm (particulate colorant dispersion A).

[0052]

As 100 parts amount of a particulate colorant dispersion, 20 parts of pigment red 238 was treated in the presence of 2.5 parts of alkylbenzene sulfonate by means of a sand grinder mill for 6 hours to obtain the particulate colorant dispersion. The resulting dispersion had a solid concentration of 20%, and an average particle diameter determined by UPA of 180 nm (particulate colorant dispersion B).

[0053]

As 100 parts of a particulate colorant dispersion, 20 parts of pigment yellow 74 was treated in the presence of 7 parts of polyoxyethylene alkylphenyl ether by means of a sand grinder mill for 6 hours to obtain the particulate colorant dispersion. The resulting dispersion had a solid concentration of 20%, and an average particle diameter determined by UPA of 300 nm (particulate colorant dispersion C).

[0054]

<Preparation of particulate charge control agent dispersion>

As 100 parts of a particulate charge control agent dispersion, 20 parts of 4,4'-methylenebis[2-[N-(4-chlorophenyl)amide]-3-hydroxynaphthalene] was dispersed in the presence of 4 parts of alkyl naphthalene sulfonate by means of a sand grinder mill to obtain the particulate charge control agent dispersion. The resulting dispersion had a solid concentration of 24%, and an average particle diameter determined by UPA of 200 nm (particulate charge control agent dispersion A).

[0055]

[Table 4]

[Example 1]

Primary polymer particle dispersion A	90 parts (as solid content)
Particulate resin dispersion A	10 parts (as solid content)
Particulate colorant dispersion A	6.7 parts (as solid content)
Particulate charge control agent dispersion A	2 parts (as solid content)
Aqueous solution of S-DBS	0.5 part (as solid content)

[0056]

The above-described respective components were mixed in such an order as described below.

To primary polymer particle dispersion A was added aqueous solution of S-DBS, which were uniformly mixed. Then particulate colorant dispersion A was added to the resulting mixture, which were also uniformly mixed.

Aqueous aluminum sulfate (0.6 part as solid content) was added at 30°C to the mixture dispersion thus obtained with stirring the same by means of an anchor blade equipped with a baffle. After the addition of the aqueous aluminum sulfate, the mixed dispersion had an average particle diameter of 2 μm . Thereafter, the mixed dispersion was heated to 55°C and the mixed dispersion was kept at that temperature for 1 hour, further heated to 58°C where it was kept for 1 hour. Thereafter, particulate charge control agent dispersion A, particulate resin dispersion A and aqueous aluminum sulfate (0.1 part as the solid content) were successively added. After keeping the resulting mixture for 1.5 hours, 10% aqueous solution of S-DBS (3 parts as solid content) was added thereto. The resulting mixture was heated to 95°C where the mixture was kept for 4 hours. Successively, the mixture obtained was cooled, filtered through a Kiriya funnel, washed with water, and then freeze-dried to obtain a toner (toner A).

[0057]

To 100 parts of the toner was added 0.6 part of silica

having been subjected to hydrophobic surface treatment with stirring to obtain a toner for development (toner A for development).

Toner A obtained had a volume average particle diameter determined by Coal Tar Counter of 7.4 μm . In the resulting toner, the portion having a volume particle diameter of 5 μm or less was 1.7%. While the portion having a volume particle diameter of 15 μm or more was 0.3%. The ratio of the volume average particle diameter and the number average particle diameter was 1.09. Thus, the particle size distribution was extremely desirable.

[0058]

The fixability of toner A for development was evaluated. As the result, at a fixing rate of 120 mm/s, the toner was fixed at a temperature of from 180°C to 220°C, and at a fixing rate of 30 mm/s, the toner was fixed at a temperature of from 150°C to 180°C. The electrified quantity of toner A determined by Color Page Presto was -8 $\mu\text{C/g}$ and the electrified quantity of toner A for development was -18 $\mu\text{C/g}$.

[0059]

[Example 2]

Toner B and toner B for development were obtained according to the same manner as in Example 1 except that the particulate colorant dispersion A was changed to particulate colorant dispersion B. Toner B obtained had a volume average

particle diameter of 7.5 μm . In the resulting toner, the portion having a volume particle diameter of 5 μm or less was 1.5%. While the portion having a volume particle diameter of 15 μm or more was 0.2%. The ratio of the volume average particle diameter and the number average particle diameter was 1.11. Thus, the particle size distribution was extremely desirable.

[0060]

The fixability of toner B for development was evaluated. As the result, at a fixing rate of 120 mm/s, the toner was fixed at a temperature of from 200°C to 220°C, and at a fixing rate of 30 mm/s, the toner was fixed at a temperature of from 160°C to 190°C. The electrified quantity of toner B determined by Color Page Presto was -20 $\mu\text{C/g}$ and the electrified quantity of toner B for development was -25 $\mu\text{C/g}$.

[0061]

[Example 3]

Toner C and toner C for development were obtained according to the same manner as in Example 1 except that the particulate colorant dispersion A was changed to particulate colorant dispersion C. Toner C obtained had a volume average particle diameter of 7.6 μm . In the resulting toner, the portion having a volume particle diameter of 5 μm or less was 1.5%. While the portion having a volume particle diameter of 15 μm or more was 0%. The ratio of the volume average particle diameter and the number average particle diameter was 1.09.

Thus, the particle size distribution was extremely desirable.

[0062]

The fixability of toner C for development was evaluated. As the result, at a fixing rate of 120 mm/s, the toner was fixed at a temperature of from 160°C to 220°C, and at a fixing rate of 30 mm/s, the toner was fixed at a temperature of from 140°C to 220°C. The electrified quantity of toner C determined by Color Page Presto was -3 $\mu\text{C/g}$ and the electrified quantity of toner C for development was -21 $\mu\text{C/g}$.

[0063]

[Table 5]

[Example 4]

Primary polymer particle dispersion B	100 parts (as solid content)
Particulate resin dispersion B	21 parts (as solid content)
Particulate colorant dispersion A	6.7 parts (as solid content)
Particulate charge control agent dispersion A	0.1 part (as solid content)

[0064]

The above-described respective components were mixed in such an order as described below.

To primary polymer particle dispersion B was added particulate colorant dispersion A, which were uniformly mixed. Aqueous solution of NaCl (10 parts as solid content) was added at 20°C to the mixture dispersion thus obtained with stirring by means of an anchor blade. Thereafter, the mixed dispersion was heated to 45°C and the mixed dispersion was kept at that temperature for 1 hour, further heated to 95°C where it was kept for 5 hours. Successively, the mixture obtained was cooled, to obtain toner particles.

[0065]

Into a glass reaction vessel equipped with an agitator, a heating condenser, a concentrating apparatus and an apparatus for charging starting materials and auxiliaries were charged the above-described toner particles 100 parts and stirred. Then particulate charge control agent dispersion A and particulate resin dispersion B were added thereto, which were kept at 45°C for 2 hours. Successively, the mixture obtained was cooled, filtered through a Kiriya funnel, washed with water, and then freeze-dried to obtain toner (toner D). To 100 parts of the toner obtained was added 0.6 part of silica having been subjected to hydrophobic surface treatment with stirring to obtain toner for development (toner D for development).

[0066]

Toner D obtained had a volume average particle diameter

of 7.1 μm . The ratio of the volume average particle diameter and the number average particle diameter was 1.20.

The fixability of toner D for development was evaluated. As the result, at a fixing rate of 120 mm/s, the toner was fixed at a temperature of from 110°C to 200°C. The electrified quantity of toner D for development determined by Phaser was -20 $\mu\text{C/g}$.

[0067]

[Example 5]

Toner E and toner E for development were obtained according to the same manner as in Example 4 except that the primary polymer particle dispersion B was changed to primary polymer particle dispersion C.

Toner E obtained had a volume average particle diameter of 6.8 μm . The ratio of the volume average particle diameter and the number average particle diameter was 1.05.

The fixability of toner E for development was evaluated. As the result, at a fixing rate of 120 mm/s, the toner was fixed at a temperature of from 115°C to 200°C. The electrified quantity of toner E for development determined by Phaser was -19 $\mu\text{C/g}$.

[0068]

[Example 6]

Toner F and toner F for development were obtained according to the same manner as in Example 4 except that the

primary polymer particle dispersion B was changed to primary polymer particle dispersion D and the amount of the particulate resin dispersion B was changed to 10 parts.

Toner F obtained had a volume average particle diameter of 6.3 μm . The ratio of the volume average particle diameter and the number average particle diameter was 1.04.

The fixability of toner F for development was evaluated. As the result, at a fixing rate of 120 mm/s, the toner was fixed at a temperature of from 120°C to 200°C. The electrified quantity of toner F for development determined by Phaser was -27 $\mu\text{C/g}$.

[0069]

[Comparative Example 1]

Toner G and toner G for development were obtained according to the same manner as in Example 3 except that the particulate resin dispersion A was not added. Toner G obtained had a volume average particle diameter of 7.1 μm .

The fixability of toner G for development was evaluated. As the result, at a fixing rate of 120 mm/s, the toner was fixed at a temperature of from 130°C to 220°C, and at a fixing rate of 30 mm/s, the toner was fixed at a temperature of from 112°C to 182°C. The electrified quantity of toner G was determined by Color Page Presto. Toner G was not negatively charged. The electrified quantity of toner G for development was -1 $\mu\text{C/g}$.

[0070]

[Comparative Example 2]

Toner H and toner H for development were obtained according to the same manner as in Example 6 except that the particulate resin dispersion A was not used. Toner H obtained had a volume average particle diameter of 6.0 μm and the volume average particle diameter/the number average particle diameter of 1.02.

The fixability of toner H for development was evaluated. As the result, at a fixing rate of 120 mm/s, the toner was fixed at a temperature of from 120°C to 200°C. The electrified quantity of toner H for development was determined by Phaser. Toner H for development was not negatively charged.

[0071]

[Effect of the Invention]

In accordance with the present invention, can be provided a polymerized toner having excellent fixability at a low temperature and electrification.. Further, the polymerized toner according to the present invention has a small particle diameter and sharp particle size distribution and, therefore, suitable for the formation of an image having a high resolution.

[Designation of Document] Abstract

[Abstract]

[Problem] Provision of a polymerized toner having excellent fixability at a low temperature and electrification.

[Means for Resolution] A toner for the development of an electrostatic image wherein particulate resin is adhered or fixed over an agglomerate containing at least primary polymer particles, characterized in that said primary polymer particles have a structure substantially comprising a wax encapsulated therein.

[Selected Drawing] None